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<b>(21) International Application Number:</b> PCT/US94/11452 <b>(22) International Filing Date:</b> 12 October 1994 (12.10.94)  <b>(30) Priority Data:</b> 08/146,652                      2 November 1993 (02.11.93)                      US  <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).  <b>(72) Inventors:</b> SCHULTZ, Craig, E.; 400 Timbercreek Drive #304, Richwood, TX 77531 (US). BERTRAM, James, L.; 115 Southern Oak Drive, Lake Jackson, TX 77566 (US). CLAY, William, A.; 232 Trailride Road, Angleton, TX 77515 (US). XIA, Guang-Ming; 111 Silver Lace Street, Lake Jackson, TX 77566 (US). GAN, Joseph; 100, route du Polygone, F- 67100 Strasbourg (FR).  <b>(74) Agent:</b> MAURER, Charles, J., III; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641- 1967 (US).		<b>(81) Designated States:</b> CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CURE INHIBITED EPOXY RESIN COMPOSITIONS AND LAMINATES PREPARED FROM THE COMPOSITIONS  <b>(57) Abstract</b>  In summary, the invention is related to the discovery of a class of compounds which inhibits the reaction of a polyepoxide with a curing agent at low temperatures. An epoxy resin composition contains a) a polyepoxide; b) an amine or amide curing agent for the polyepoxide; c) at least about 15 meq (per equivalent of polyepoxide) of a catalyst for the reaction of the polyepoxide with the curing agent; and d) a cure inhibitor selected such that: (1) at about 171 °C the composition has a gel time that is at least about 50 percent longer than a similar composition without the inhibitor, and (2) at about 175 °C and higher the composition cures in no more than about 50 minutes. The composition can cure rapidly with high crosslink density because it has a high catalyst loading, but the inhibitor lengthens the gel time to permit laminating and other processing.		

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## CURE INHIBITED EPOXY RESIN COMPOSITIONS AND LAMINATES PREPARED FROM THE COMPOSITIONS

This invention relates to epoxy resin compositions, and particularly to compositions useful for making electrical laminates.

- 5           Epoxy resin compositions are commonly used to make electrical laminates according to the following process steps:
- (1)           a substrate is impregnated with an epoxy resin composition containing the resin, a curing agent for the resin and a catalyst for the curing reaction. The concentration of catalyst is usually about 0.1 parts catalyst per 100 parts epoxy resin (by weight). Generally the composition contains one or more organic solvents in which the various components are dissolved or dispersed, with a solid content of between 45 and 90 percent. The substrate is usually a cloth of woven or unwoven fibers, and particularly glass fibers. The composition is usually applied by immersing the substrate in a bath of the composition, but it may be applied by other methods, such as spraying or rolling.
- 10           (2)           The impregnated substrate is passed through a heated zone to remove the solvent by evaporation, and optionally to partially-cure the resin composition. The process of partially-curing the resin is called "B-staging." The partially-cured product is called a prepreg.
- 20           (3)           If the prepreg is not intended for immediate use, it is cooled and stored at a temperature less than 50°C.
- (4)           One or more prepregs are stacked with one or more sheets of electrical conductor and pressed at elevated temperature to cure the composition and form a laminate. In this curing process the resin coating on the glass cloth flows and mixes with the coating on adjacent glass clothes thereby resulting in a fusing of the glass layers together, via the cured epoxy resin. The conductor is usually a sheet of copper, although gold or other conductors may also be used.
- 25           (5)           Optionally, the cured laminate is post-treated by exposing it to high temperature. Frequently, the epoxy resin composition is formulated by one manufacturer, the prepreg is made by a second, and the laminate is made by a third. Therefore, the formulated composition must be shelf-stable until it is used to make prepreg, and the prepreg must stop curing when it is cooled and remain shelf-stable until it is used by the laminator. Many common formulations are not sufficiently stable. If stabilizers are added, they often slow the curing time of the resin.
- 30           It is known to use boric acid as an inhibitor for the reaction. See, for example, Bertram et al., EPO Application 91304277.6, published as EPO Publication 0458502 on November 27, 1991. Compositions that contain boric acid cure rapidly at curing temperatures,

but have good shelf-stability both as formulations and in prepregs. It would be desirable to identify other inhibited compositions that will provide similar good results.

One aspect of the present invention is an epoxy resin composition comprising:

- a) a polyepoxide;
- 5 b) an amine or amide curing agent for the polyepoxide; and
- c) a catalyst for the reaction of the polyepoxide with the curing agent,

characterized in that:

- (1) the concentration of catalyst is at least about 15 meq per equivalent of polyepoxide; and
- 10 (2) the composition further contains a cure inhibitor which is a Lewis acid other than boric acid and which is selected such that:
  - (1) at about 171°C the composition has a stroke cure gel time that is at least about 50 percent longer than a similar composition without the inhibitor, and
  - 15 (2) at temperatures of 175°C or higher the composition cures in no more than about 60 minutes.

The test for stroke-cure gel time and curing are described hereinafter.

A second aspect of the present invention is a process for making a prepreg comprising the steps of:

- 20 (1) impregnating a substrate with a curable composition as previously described;
- (2) drawing off solvent from the composition and partially curing the composition at a temperature of 80°C to 190°C to form a B-staged prepreg; and
- (3) cooling the B-staged prepreg and storing it at a temperature less than 50°C.
- 25 A third aspect of the present invention is a prepreg comprising:
  - (1) a fiber-containing substrate; and
  - (2) a partially-cured curable composition as previously described impregnated upon the substrate.

The invention has several advantages. The composition can be exposed to  
30 temperatures at which any solvent present is removed by evaporation without significant curing of the epoxy resin. Preferably this composition is stable for more than two days, more preferably stable for more than two months, and most preferably stable for six months or more, at ambient temperatures. The B-staged compositions are also stable for similar periods at about room temperature. However, the compositions also contain a high concentration of  
35 catalyst, so that they cure quickly at laminating temperatures. Additionally, the compositions frequently cure to provide a laminate with a higher glass-transition temperature than equivalent compositions made without the high catalyst concentration and inhibitor.

Polyepoxides used in the present invention are compounds or mixtures of compounds containing on average more than one epoxy moiety. Polyepoxide as used herein includes partially advanced epoxy resins that is, the reaction of a polyepoxide and a curing agent, wherein the reaction product has an average of at least one unreacted epoxide unit per molecule. The polyepoxide preferably contains 2 to 12 epoxy groups per molecule.

For example, the polyepoxide may be a poly(glycidyl ether) of a polyhydric phenol, that is, compounds having an average of more than one aromatic hydroxyl group per molecule such as, for example, dihydroxy phenols, biphenols, bisphenols, halogenated biphenols, halogenated bisphenols, alkylated biphenols, alkylated bisphenols, hydrogenated bisphenols, trisphenols, phenol-aldehyde novolac resins, halogenated and/or substituted phenol-aldehyde novolac resins, phenol-hydrocarbon resins and halogenated or alkylated variations of those resins, or any combination thereof. Polyglycidyl ethers of the following polyhydric phenols are more preferred: bisphenols; halogenated bisphenols; hydrogenated bisphenols; novolac resins; and polyalkylene glycols.

The preparation of such compounds is well known in the art. See Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 9, pp. 267-289. Examples of preferred epoxy resins and their precursors are described in Davis et al., U.S. Patent 4,251,594 (February 17, 1981); Berman et al., U.S. Patent 4,604,317 (August 5, 1986); Wang, U.S. Patent 4,672,103 (June 9, 1987); Bogan, U.S. Patent 4,710,429 (December 1, 1987); Walker et al., U.S. Patent 5,066,735 (November 19, 1991) (individually and in the claimed mixtures); Koenig et al., U.S. Patent 5,112,932 (May 12, 1992); and Bertram et al., U.S. Patent 5,169,473 (December 8, 1992).

Highly preferable epoxy resins include, for example, the diglycidyl ethers of resorcinol, catechol, hydroquinone, biphenol, bisphenol A, bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl ethane), bisphenol F, bisphenol K, tetrabromobisphenol A, phenol-formaldehyde novolac resins, alkyl substituted phenol-formaldehyde resins, phenol-hydroxybenzaldehyde resins, cresol-hydroxybenzaldehyde resins, dicyclopentadiene-phenol resins, dicyclopentadiene-substituted phenol resins tetramethylbiphenol, tetramethyl-tetrabromobiphenol, tetramethyltribromobiphenol, tetrachlorobisphenol A, or any combination thereof.

Other preferable polyepoxides are the glycidyl ethers of compounds having an average of more than one aliphatic hydroxyl group per molecule such as, for example, aliphatic diols, polyether diols, polyether triols, polyether tetrols and any combination thereof. Also suitable are the alkylene oxide adducts of compounds containing an average of more than one aromatic hydroxyl group per molecule such as, for example, the ethylene oxide, propylene oxide, or butylene oxide adducts of dihydroxy phenols, biphenols, bisphenols, halogenated bisphenols, alkylated bisphenols, trisphenols, phenol-aldehyde novolac resins, halogenated phenol-aldehyde novolac resins, alkylated phenol-aldehyde novolac resins, hydrocarbon-

phenol resins, hydrocarbon-halogenated phenol resins, or hydrocarbon-alkylated phenol resins, or any combination thereof.

In one embodiment polyepoxides refers to an advanced epoxy resin which is the reaction product of one or more polyepoxides, as described previously, with one or more polyhydroxy hydrocarbons or a halogenated derivative thereof. Such polyhydroxy hydrocarbons have been described previously. Alternatively, a polyepoxide can be reacted with a carboxyl-substituted hydrocarbon. A carboxyl substituted hydrocarbon is a compound with a hydrocarbon backbone and one or more carboxyl moieties, preferably more than one, and most preferably two. Preferably such compounds correspond to Formula (I);



wherein  $R^5$  is a  $C_{1-40}$  hydrocarbyl moiety (optionally containing oxygen along the backbone), and  $u$  is an integer of one or greater.  $R^5$  is preferably a  $C_{1-40}$  straight- or branched-chain alkane or alkene, optionally containing oxygen. Preferably  $u$  is 1 to 4, and most preferably 2. Fatty acids and fatty acid dimers are among the useful carboxylic acid substituted hydrocarbons. Included in the fatty acids are caproic acid, caprylic acid, capric acid, octanoic acid, versatic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, erucic acid, pentadecanoic acid, margaric acid, arachidic acid, and dimers thereof.

In another embodiment, the polyepoxide is the reaction product of a polyepoxide and a compound containing more than one isocyanate moiety, a polyisocyanate. Preferably the polyepoxide is an epoxy-terminated polyoxazolidone. It preferably has from 5 to 30, more preferably 5 to 20, most preferably 10 to 20 weight percent isocyanate content and has from 50 to 100 percent of the original isocyanate groups converted to oxazolidone rings and from 0 to 50 percent of the original isocyanate groups converted to isocyanurate rings whenever prepared according to the process described herein. Epoxy-terminated polyoxazolidone (isocyanate modified epoxy resin) are preferably prepared by the process described in Koenig, U.S. Patent 5,112,932 (May 12, 1992).

Amine- and amide-containing curing agents in the present invention are compounds that contain on average more than one active hydrogen atom, wherein the active hydrogen atoms are bonded to the same nitrogen atom or to different nitrogen atoms. Examples of suitable curing agents include: compounds that contain a primary amine or amide moiety and compounds that contain two or more primary or secondary amine or amide moieties linked to a common central organic moiety. Examples of suitable amine-containing curing agents include: diethylene triamine, triethylene tetramine, dicyandiamide, melamine, pyridine, cyclohexylamine, benzyldimethylamine, benzylamine, diethylaniline, triethanolamine, piperidine, N,N-diethyl-1,3-propane diamine, and soluble adducts of amines and polyepoxides and their salts, such as described in U.S. Patents 2,651,589 and 2,640,037.

Polyamides are preferably the reaction product of a polyacid and an amine. Examples of polyacids used in making these polyamides include, among others, 1,10-decanedioic acid, 1,12-dodecanedienedioic acid, 1,20-eicosadienedioic acid, 1,14-tetradecanedioic acid, 1,18-octadecanedioic acid and dimerized and trimerized fatty acids.

5 Amines used in making the polyamides include preferably the aliphatic and cycloaliphatic polyamines as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-diamino-butane, 1,3-diaminobutane, hexamethylene diamine and 3-(N-isopropylamino)propylamine. Especially preferred polyamides are those derived from the aliphatic polyamides containing no more than 12 carbon atoms and polymeric fatty acids  
10 obtained by dimerizing and/or trimerizing ethylenically unsaturated fatty acids containing up to 25 carbon atoms. These preferred polyamides preferably have a viscosity between 10 and 750 poises at 40°C, and preferably 20 to 250 poises at 40°C. Preferred polyamides also have amine values of 50 to 450.

Preferred curing agents are aliphatic polyamines, polyglycoldiamines,  
15 polyoxypropylene diamines, polyoxypropylenetriamines, amidoamines, imidazolines, reactive polyamides, ketimines, araliphatic polyamines (that is, xylylenediamine), cycloaliphatic amines (that is, isophoronediamine or diaminocyclohexane) menthane diamine, 3,3-dimethyl-4,4-diamino-dicyclohexylmethane, heterocyclic amines (aminoethyl piperazine), aromatic polyamines, (methylene dianiline), diamino diphenyl sulfone, mannich base, phenalkamine  
20 and N,N'N''-tris(6-aminoethyl) melamine. The most preferred curing agents are cyanamide, dicyandiamide, and its derivatives, diaminodiphenyl sulfone and methylene dianiline.

The ratio of curing agent to epoxy resin is preferably suitable to provide a fully cured resin. The amount of curing agent which may be present may vary depending upon the particular curing agent used. The curable composition preferably contains from 0 to 150 parts  
25 of curing agent per hundred parts of resin (phr), more preferably from 0.5 to 30 phr curing agent, more highly preferably from 1.0 to 10.0 phr curing agent, and most preferably from 2 to 4 phr curing agent. The equivalent ratio of epoxy moieties to curing moieties is preferably at least 0.8:1 and more preferably at least 0.9:1. The equivalent ratio is preferably no more than 1.5:1 and more preferably no more than 1.2:1.

30 Catalysts useful in this invention are those catalysts which catalyze the reaction of a polyepoxide with a curing agent, and which remains latent in the presence of the inhibitor at lower temperatures. Examples of curing catalysts are described in Walker et al., U.S. Patent 4,868,059 (September 19, 1989) and Bertram et al., U.S. Patent 5,169,473 (December 8, 1992).

The catalyst preferably contains amine, phosphine, heterocyclic nitrogen,  
35 ammonium, phosphonium, arsonium or sulfonium moieties, more preferably contains heterocyclic nitrogen or amine-containing moieties and most preferably contains heterocyclic nitrogen-containing moieties. Preferable heterocyclic secondary and tertiary amines or nitrogen-containing compounds which can be employed herein include, for example,

imidazoles, benzimidazoles, imidazolidines, imidazolines, oxazoles, pyrroles, thiazoles, pyridines, pyrazines, morpholines, pyridazines, pyrimidines, pyrrolidines, pyrazoles, quinoxalines, quinazolines, phthalazines, quinolines, purines, indazoles, indoles, indolazines, phenazines, phenarsazines, phenothiazines, pyrrolines, indolines, piperidines, piperazines, substituted variations thereof and combinations thereof. Especially preferred are the alkyl-substituted imidazoles; 2,5-chloro-4-ethyl imidazole; and phenyl substituted imidazoles, and mixtures thereof. Even more preferred are 2-methyl imidazole; 2-ethyl, 4-methyl imidazole; 1,2-dimethylimidazole; and 2-phenyl imidazole. Most preferred is 2-methyl imidazole.

Among preferred tertiary amines that may be used as catalysts are those mono- or polyamines having an open chain or cyclic structure which have all of the amine hydrogen replaced by suitable substituents, such as hydrocarbon radicals, and preferably aliphatic, cycloaliphatic or aromatic radicals. Examples of these amines include, among others, methyl diethanol amine, triethylamine, tributylamine, dimethyl benzylamine, triphenylamine, tricyclohexyl amine, pyridine, and quinoline. Preferred amines are the trialkyl, tricycloalkyl and triaryl amines, such as triethylamine, triphenylamine, tri(2,3-dimethylcyclohexyl)amine, and the alkyl dialkanol amines, such as methyl diethanol amines and the trialkanolamines such as triethanolamine. Weak tertiary amines, for example, amines that in aqueous solutions give a pH less than 10, are particularly preferred. Especially preferred tertiary amine accelerators are benzyldimethylamine and tris-dimethylaminomethyl phenol.

The catalyst should be present in quantities of at least 15 meq of catalyst for each equivalent of epoxy resin. The concentration of catalyst is preferably at least about 20 meq per equivalent of epoxy resin. It is preferably no more than about 50 meq per equivalent and more preferably no more than about 25 meq per equivalent. The higher than normal catalyst loadings make it possible to have very rapid cure at higher temperatures. When the catalyst is 2-methylimidazole, the concentration is preferably at least about 0.3 phr (parts catalyst per 100 parts resin, by weight) and more preferably at least about 0.4 phr. The concentration is preferably no more than about 1 phr, and more preferably no more than about 0.5 phr.

The composition contains a Lewis acid curing inhibitor, which forms a complex with the catalyst. The complexes exist in equilibrium with the uncomplexed catalyst and complexing agent. At any given moment a portion of the catalyst is complexed with the complexing agent and a portion is not. The portion of free catalyst is dependent upon several variables, including the complexing agent, its concentration relative to the catalyst, the temperature of the mixture and the solvents used to dissolve the boric acid and resin formulations.

The inhibitor and its concentration are selected such that the resin does not gel too fast at temperatures that are ordinarily used to impregnate and laminate a composite. (Stroke-cure gel time of a resin can be determined by test DOWM101210-TE92A, which is described in the working examples). The stroke-cure gel time of the resin containing the



inhibitor at about 171°C is preferably at least about 50 percent longer than the gel time of a similar composition containing no inhibitor. The stroke-cure gel time is preferably at least about 100 percent longer, and more preferably at least about 200 percent longer. At about 171°C, the stroke-cure gel time of the composition is preferably more than 70 seconds, highly  
5 preferably more than 100 seconds, more preferably more than 200 seconds, more highly preferably more than 250 seconds, and most preferably more than 300 seconds. It is desirable to keep the gel time as long as possible, but it is seldom more than about 1000 seconds for useful compositions. The composition preferably exhibits no significant change in its gel time when stored at 20°C to 25°C or less over a period of at least 2 days, more preferably at least  
10 about 10 days and most preferably at least about 30 days.

The inhibitor should also dissociate from the catalyst at curing temperatures, so that the excess catalyst causes more rapid curing than compositions with an ordinary catalyst content and no inhibitor. A sample is considered cured when its glass-transition temperature changes by no more than 3°C between first and second testing by IPC test method: 2.4.25  
15 (revision B dated 12/87) as described in the testing methods section hereinafter. (This test may not meet every user's definition of a "fully cured" resin, since different users may have different performance criteria that a cured resin must meet. Some users may require further curing to meet all performance criteria. However, the test does establish that under curing conditions there is at least as much catalyst activity as - and preferably more catalyst activity  
20 than - a system with ordinary catalyst loadings and no inhibitor). The composition should be cured in no more than about 60 minutes at temperatures of about 175°C. The composition is highly preferably cured in no more than about 50 minutes, preferably in no more than about 45 minutes, more preferably in no more than about 30 minutes, and most preferably in no more than about 20 minutes.

25 Examples of suitable inhibitors include halides, oxides, hydroxides and alkoxides of zinc, tin, titanium, cobalt, manganese, iron, silicon, boron, aluminum and similar compounds (other than boron halides or boric acid) - for instance boroxines (such as trimethoxyboroxine), boron oxide, alkyl borates, zinc halides (such as zinc chloride) and other Lewis acids that tend to have a relatively weak conjugate base. When the formulation is intended for use in electrical  
30 laminates, then the inhibitor preferably contains no significant levels of halide. Boric acid as used herein includes metaboric acid and boric anhydride.

The molar ratio of catalyst to inhibitor is selected to provide the results previously described. The optimum ratio may vary from catalyst to catalyst and from inhibitor to inhibitor. In most cases, the molar ratio of inhibitor to catalyst is preferably at least 0.6:1, more preferably  
35 at least 0.75:1 and most preferably at least 1:1. The molar ratio of inhibitor to catalyst is preferably no more than 3:1, more preferably no more than 1.4:1 and most preferably no more than 1.35:1.

For example, the preferred molar ratio of boric acid to imidazole compound is from 0.85:1 to 1.12:1 while the most preferred ratio is in the range of from 0.93:1 to 1.1:1. For phosphonium compounds, the preferred ratio is from 0.95:1 to 1.35:1, more preferably from 1.1:1 to 1.25:1 moles of acid per mole of phosphonium compound. When the amount of boric acid is less than about 0.6 mole per mole of imidazole the catalyst is less latent and begins to approach the reactivity of the original imidazole prior to reaction with the acid or acid salt. When the amount of boric acid is more than about 1.4 moles per mole of phosphonium, the catalyst becomes less latent. When the amount of acid or acid salt is more than about 1.14 moles per mole of imidazole, the catalyst becomes less latent.

The inhibitor and catalysts may be separately added to the compositions of this invention, or may be added as a complex. The complex is formed by contacting and intimately mixing a solution of the inhibitor with a solution of the catalyst. Optionally, an acid having a weak nucleophilic anion may be present. Such contacting generally is performed at ambient temperature, although other temperatures may be used, for example, temperatures of from 0°C to 100°C, more preferably from 20°C to 60°C. The time of contacting is that sufficient to complete formation of the complex, and depends on the temperature used, with from 1 to 120 minutes preferred, and 10 to 60 minutes more preferred. Preferred solvents for the catalyst and the inhibitor are polar solvents, with alcohols being preferred. Lower alcohols are even more preferred, with methanol most preferred.

The catalysts can be employed alone or in combination with other catalysts, preferably catalytic products resulting from reacting the onium or amine compounds or a combination thereof with an inorganic acid containing a weak nucleophile. By the term "weak nucleophile" or "weak nucleophilic," it is meant that the material has a nucleophilicity value "n" of greater than zero and less than 2.5 as described by C. G. Swain and C. B. Scott in J. Am. Chem. Society, Vol. 75, p. 141 (1953). Particularly suitable inorganic acids having a weak nucleophilic anion or weak nucleophile include, for example, fluoboric acid, fluoarsenic acid, fluoantimonic acid, fluophosphoric acid, chloroboric acid, chloroarsenic acid, chloroantimonic acid, chlorophosphoric acid, perchloric acid, chloric acid, bromic acid, iodic acid and any combination thereof. Most particularly the acid is fluoboric acid.

The composition of the present invention may optionally be a powder without solvent, but it is preferably in a solution or dispersion with a solvent. Preferably the concentration of solids in the solvent is at least about 50 percent and no more than about 75 percent solids. The solvent is preferably an organic solvent, such as ketones, alcohols, glycol ethers, aromatic hydrocarbons and mixtures thereof. Preferred examples of solvents included methylethyl ketone, methylisobutylketone, propylene glycol methylether, ethylene glycol methylether, methyl amyl ketone, methanol, isopropanol, toluene, xylene and dimethylformamide. Examples of suitable solvents are described in Berman et al., U.S. Patent 4,756,954 (July 12, 1988). A single solvent may be used, but in many applications a separate solvent is used for

each component. It is preferable that the various solvents used be miscible with one another. Preferred solvents for the epoxy resins are ketones, including acetone and methylethylketone. Preferred solvents for the curing agents are slightly polar solvents, amides, for example, DMF, ether alcohols such as methyl, ethyl, propyl or butyl ethers of ethylene glycol, diethylene glycol, 5 propylene glycol or dipropylene glycol, for example, ethylene glycol monomethyl ether, or 1-methoxy-2-propanol. The catalysts and inhibitors are preferably dissolved in polar solvents, in particular alcohols, preferably lower alkanols and most preferably methanol.

The compositions of the present invention may be used to make electrical laminates, as previously described. Examples of appropriate substrates include fiber-containing 10 materials such as cloth, mesh, web or fibers. Preferably, such materials are made from glass, fiberglass, paper, plastics such as aromatic polyamides and graphite. Preferred materials include glass or fiberglass, in cloth or web form. Other additives may also be present including fillers, dyes, pigments, surfactants and flow control agents.

B-staging may be carried out in a single temperature stage, or in multiple 15 temperature stages. Optionally, the coated reinforcing materials are passed through a heated zone at a temperature sufficient to cause the solvents to evaporate, but below the temperature which the polyepoxide undergoes significant cure during the residence time in the heated zone. The residence time of the coated reinforcing material in the heated zone is preferably from 0.5 to 15 minutes, more preferably from 1 to 10 minutes, and most preferably from 1.5 to 20 5 minutes. Preferable temperatures of such zone are from 80°C to 230°C, more preferably from 100°C to 200°C, and most preferably from 140°C to 190°C. Preferably there is a means in the heated zone to remove the solvent, either by passing an inert gas through the oven, or drawing a slight vacuum on the oven. In many embodiments the coated materials are exposed to zones of increasing temperature. The first zones are designed to cause the solvent to volatilize so it 25 can be removed. The latter zones are designed to result in partial cure of the polyepoxide.

The inhibited catalysts of the present invention are latent at low temperatures, meaning that the curable resin will substantially stop curing after it is B-staged if the curable resin is cooled down, preferably to below 50°C and more preferably to about room temperature (20°C to 25°C). The minimum temperature is not critical, but prepregs are 30 preferably stored at at least -10°C and more preferably at least 10°C. The B-staged resin is then storage stable, preferably for at least about 10 days, more preferably for at least about 20 days, and most preferably for at least about 30 days. This makes it possible to interrupt curing of prepregs after B-staging, to ship or store the B-staged prepregs until they are needed, and to cure them to make laminates at a later time.

35 One or more sheets of prepreg are preferably processed into laminates with one or more sheets of electrically-conductive material such as copper. Before being cured the parts may be cut and stacked or folded and stacked into a part of desired shape and thickness. The pressures are preferably from 1 to 200 kg/cm<sup>2</sup>, and more preferably from 10 to 100 kg/cm<sup>2</sup>. The

temperature is preferably between 100°C and 190°C, more preferably between 120°C and 180°C, and most preferably between 140°C and 175°C. The residence times are preferably from 10 minutes to 120 minutes, more preferably from 20 to 90 minutes, and most preferably from 30 to 50 minutes.

5                    One embodiment of such a process is known as a continuous process. In such a process, the reinforcing material is taken from the oven and appropriately arranged into the desired shape and thickness and pressed at very high temperatures for short times. Such high temperatures are from 180°C to 250°C, more preferably 190°C to 210°C, at times of 1 to 10 minutes and from 2 to 5 minutes. Such high speed pressing allows for the more efficient  
10 utilization of processing equipment. In such embodiments the preferred reinforcing material is a glass web or woven cloth.

                    The post-cure is usually performed at from 130°C to 200°C for from 20 to 200 minutes. This post cure step may be performed in a vacuum to remove any components which may volatilize.

15                    The ultimate coated reinforced parts prepared from the composition of this invention often demonstrate a higher T<sub>g</sub> than where the compositions not within the scope of this invention are used. In some embodiments the T<sub>g</sub> is at least 5°C higher than parts prepared similarly using conventional resins. More preferably the T<sub>g</sub> is increased by at least 10°C. For instance, the glass-transition temperature of cured resin made from brominated bisphenol A  
20 epoxy resin and dicyanodiamide is preferably at least 140°C and more preferably at least about 144°C, as measured by differential scanning calorimetry (DSC). The parts prepared using the composition of this invention, demonstrate a higher solvent resistance, for example, demonstrate a pick-up of less than 1.0 percent N-methyl pyrrolidone. It is theorized, without intending to be bound, that these differences result from higher crosslink density, due to the  
25 higher catalyst loading.

                    Furthermore such parts exhibit a higher thermal performance as there is little or no solvent entrapped. The formulations of this invention preferably exhibit longer gel times at certain temperatures as compared to prior art formulations.

                    The following examples are presented to illustrate the invention and are not  
30 intended to limit the scope of the claims. Unless otherwise stated all parts and percentages are by weight.

#### Testing Methods

                    The following test methods are used unless stated otherwise in the examples. Unless stated otherwise, all parts and percentages are by weight.

35

Stroke-Cure Gel Time

The test for stroke-cure gel time is available from The Dow Chemical Company as DOWM101210-TE92A (effective 26 May 1992). The published test is modified by changing the hardener/catalyst solution in paragraph (1) to reflect the actual composition to be tested. The test is summarized as follows:

- (1) A hardener/catalyst solution is made by blending one or more solvents, a curing agent and a catalyst to reflect the curable composition to be tested. The materials are blended until all the dicyandiamide is dissolved. The blend should not be stored for more than one month. (Hardener/catalyst solutions in the present application ordinarily contain 173.00 g dimethylformamide, 173.00 g propylene glycol monomethyl ether, 28.00 g dicyandiamide and a desired quantity of 2-methylimidazole - all available from Aldrich Chemical Company. However, the tester should modify the solution to reflect the actual curable composition that is being tested.)
- (2) The bottom side of a Model C01-T thermocouple (or equivalent) is pasted to a hot plate using a small amount of OMEGATHERM™ 201 thermally conductive paste, or equivalent. The thermocouple is attached to a Model 450-ATT thermocouple thermometer (or equivalent). The hot plate control is adjusted until a stable temperature of  $171^{\circ}\text{C} \pm 0.5$  is obtained. The hot plate should be located in a constant temperature area away from drafts to prevent temperature variations.
- (3) A solution that contains 40 g of resin solids is added to a 4 oz. bottle, and 15.00 g of hardener/catalyst solution is added. Inhibitor may be added to the resin, before or immediately after the hardener/catalyst solution is added. The solutions are immediately blended and are left for one hour (from the time the hardener/catalyst solution was added) before beginning the test.
- (4) A 0.5 to 0.7 mL sample of varnish is applied to the hot plate, and a timer is started. The sample rests undisturbed on the hot plate for 60 seconds  $\pm 1$ . Then the sample is stroked with a wooden spatula by pushing the resin puddle back and forth over an area of about 1 in<sup>2</sup> with the same side of the spatula in contact with the resin. The resin will thicken as it is stroked. Eventually, it becomes stringy, and then becomes a rubbery gel. That is the endpoint. The timer is stopped and the time is recorded. The resin is scraped from the plate using a razor blade being careful not to scratch the plate surface.

- (5) The test is repeated three times, and the average time to form a gel is recorded.

#### Curing

A sample is considered cured when its glass-transition temperature does not change by more than 3°C when the sample is tested twice by differential scanning calorimetry.

- 5 The glass-transition temperature method is modified from the test published by The Institute for Interconnecting and Packaging Electronic Circuits in the IPC Test Methods Manual as test 2.4.25 (revision B, dated 12/87):

- (1) A resin sample obtained from the stroke-cure gel time test is baked in a 175°C oven for the desired period of time.
- 10 (2) A specimen is cut from the sample and mounted in a standard aluminum sample pan. (The sample should not be higher than the edge of the pan). The sample is not a laminate, and so references to copper in the published test method can be ignored. An empty pan is used as a reference.
- (3) The glass-transition temperature is measured using a DuPont Model 912 differential scanning calorimeter or equivalent, starting well below the point of interest and increasing temperature at a rate of 10°C/minute until 175°C is reached. The specimen is held at 175°C for 15 minutes ( $\pm 0.5$ ) and then cooled over a period of 10 minutes to initial conditions.
- 15 (4) A second scan is carried out to a temperature of at least 180°C. The inflection points of the two scans are calculated by computer and taken to be the glass-transition temperatures of the sample. If the first and second scan are more than 3°C different, the sample is not cured.
- 20

#### Examples

##### Example 1 - Trimethoxyboroxine Inhibitor

- 25 The following mixture was agitated for one hour:

- |            |   |                                                                                                                                                             |
|------------|---|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 100 parts  | - | 80 weight percent solids solution of brominated epoxy resin (prepared from tetrabromobisphenol A and diglycidyl ether of bisphenol A) dissolved in acetone; |
| 4.5 parts  | - | 10 percent solution of                                                                                                                                      |
| 30         |   | 2-methylimidazole in dimethylformamide (DMF); and                                                                                                           |
| 27 parts   | - | 10 percent solution of dicyandiamide in a mixture of DMF and glycol ether; and                                                                              |
| 1.12 parts | - | trimethoxyboroxine.                                                                                                                                         |

- The gel time was tested as described previously. The gel time of the resin was about 249 seconds at about 171°C. The gelled resin was fully cured in no more than about 50 minutes at 175°C. After curing for 60 minutes, the glass-transition temperature of the resin was about 162°C.
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Example 2 - Trimethoxyboroxine Inhibitor

The following varnish was agitated for several hours:

- 50 parts - 80 weight percent solids solution of brominated epoxy resin (prepared from tetrabromobisphenol A and diglycidyl ether of bisphenol A) dissolved in acetone;
- 26.36 parts - epoxy resin prepared from epichlorohydrin and bisphenol A;
- 14.01 parts - tetrabromobisphenol A;
- 9.63 parts - acetone
- 7.5 parts - 10 percent solution of 2-methylimidazole in dimethylformamide (DMF); and
- 20 parts - 10 percent solution of dicyandiamide in a mixture of DMF and glycol ether; and
- 0.87 parts - trimethoxyboroxine.

The gel time was tested as described previously. The gel time of the varnish was about 226 seconds at about 171°C. The gelled varnish was fully cured in no more than about 50 minutes at 175°C.

A 6 inch by 6 inch prepreg of varnish and woven E-glass was cured according to the following conditions: Starting at a temperature of 250°F and a pressure of 20.8 psi, the temperature was increased to 350°F at 5°F/minute, and the pressure was increased to 500 psi at a rate of 20.8 psi/minute. After curing for 60 minutes at 350°F and 500 psi, the laminate was cooled to 100°F at 500 psi pressure. The glass-transition temperature of the prepreg was about 161°C.

Example 3 - Zinc Chloride Inhibitor

The following mixture was agitated for one hour:

- 100 parts - 80 weight percent solids solution of brominated epoxy resin (prepared from tetrabromobisphenol A and diglycidyl ether of bisphenol A) dissolved in acetone;
- 4.5 parts - 10 percent solution of 2-methylimidazole in dimethylformamide (DMF); and
- 27 parts - 10 percent solution of dicyandiamide in a mixture of DMF and glycol ether; and
- 4.4 parts - 10 percent solution of zinc chloride in methanol.

The gel time was tested as described previously. The gel time of the resin was about 273 seconds at about 171°C. After curing for 60 minutes, the glass-transition temperature of the resin was about 144°C.

Example 4 - Cure Time for Trimethylboroxine Inhibited System

A mixture of epoxy resin (80 percent solids in acetone), 0.45 phr of 2-methylimidazole (10 percent solids in DMF), 2.7 phr dicyandiamide (10 percent solids in

DMF/glycol ether mixture) and 1.12 phr trimethoxyboroxine (18 percent solids in ethylene glycol) was cured at 175°C for the time shown in Table XII. Two glass-transition temperatures are measured as described previously, and set out in Table I. The test shows that the resin was cured in no more than 45 minutes time.

5

Table I

	Cure Time (min)	T <sub>g</sub> 1 (°C)	T <sub>g</sub> 2 (°C)
	60	162	162
10	45	159	161
	30	152	161

#### Examples 5-16 - Alternative Cure Inhibitors

The process of Example 1 was followed, substituting the inhibitors in Table II in the quantities in Table II for the trimethylboroxine shown in Example 1. Those results are shown in Table II. (A) is not an example of the invention.

15

Table II

	Ex	Inhibitor	Quantity (phr)	Gel Time (sec)
20	5	BCl <sub>3</sub>	0.45	460
	6	TiCl <sub>4</sub>	0.80	516
	7	TiCl <sub>4</sub>	0.20	460
	8	TiCl <sub>4</sub>	0.10	300
25	9	SnCl <sub>4</sub>	0.20	366
	10	CoCl <sub>2</sub>	0.20	275
	11	CoCl <sub>2</sub>	0.10	150
	12	CrCl <sub>3</sub>	0.13	265
	13	MnCl <sub>2</sub>	0.20	322
30	14	FeCl <sub>2</sub>	0.10	198
	15	FeCl <sub>3</sub>	0.10	248
	16	SiCl <sub>4</sub>	0.20	438
	A	None	0	85

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CLAIMS:

1. An epoxy resin composition comprising
  - a) a polyepoxide;
  - b) an amin or amide curing agent for the poly .poxide; and
  - c) a catalyst for the reaction of the polyepoxide with the curing agent,5 characterized in that:
  - (1) the concentration of catalyst is at least 15 meq per equivalent of polyepoxide; and
  - (2) the composition further contains a cure inhibitor which is a Lewis acid other than boric acid and which is selected such that:
    - 10 (1) at 171°C the composition has a gel time that is at least 50 percent longer than a similar composition without the inhibitor, and
    - (2) at 175°C and higher the composition cures in no more than 60 minutes.
2. A composition as described in Claim 1 which further comprises one or more solvents.
- 15 3. A composition as described in any of the previous claims wherein the inhibitor is any halide, oxide, hydroxide or alkoxide of zinc, boron, tin, titanium, cobalt, manganese, iron, silicon or aluminum, other than a boron halide or boric acid.
4. A composition as described in any of the previous Claims wherein the inhibitor is any of boroxime, boron oxide, an alkyl borate or a zinc halide.
- 20 5. The composition as described in any of the previous claims wherein the composition contains 20 to 50 meq of catalyst per equivalent of polyepoxide.
6. A composition as described in any of the previous claims wherein the molar ratio of inhibitor to catalyst is from 0.6: 1 to 3: 1.
7. A composition as described in any of the previous claims wherein the catalyst is  
25 an imidazole compound, and the composition contains 0.3 to 1 part catalyst per 100 parts epoxy resin, by weight.
8. Use of a composition as described in any of the previous claims to make a B-staged prepreg by the process of:
  - (1) impregnating a substrate with a curable composition as described in any of the  
30 previous Claims;
  - (2) drawing off solvent from the composition and partially curing the composition at a temperature of 100°C to 190°C to form a B-staged prepreg; and
  - (3) cooling the B-staged prepreg and storing it at a temperature less than 50°C.
9. Use as described in Claim 8 which further comprises the step of:  
35 (4) pressing one or more B-staged prepreg with one or more sheets of an electrically conductive material to form a laminate and curing the curable composition in the laminate.
10. A prepreg comprising:

- (1) a fiber-containing substrate; and
- (2) a partially-cured curable composition as described in any of Claims 1-7 adhered to the substrate.

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/11452

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C08G59/18 C08G59/50 C08J5/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 117 113 (NATIONAL RESEARCH DEVELOPMENT CORPORATION) 29 August 1984 see page 7, line 27 - page 8, line 21; claims; example 10 ---	1-10
A	US,A,4 707 518 (DILIPKUMAR N. SHAH) 17 November 1987 see claims ---	1-10
A	EP,A,0 557 068 (PILKINGTON PLC) 25 August 1993 see claims -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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US-A-4707518	17-11-87	CA-A- 1276737 EP-A- 0265056 JP-A- 63314289	20-11-90 27-04-88 22-12-88
EP-A-0557068	25-08-93	GB-A- 2264260	25-08-93